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The Use of Portable Volatile Organic Compound Analyzers for Leak Detection

Battelle Columbus Labs., OH

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THE USE OF PORTABLE VOLATILE ORGANIC COMPOUND ANALYZERS FOR LEAK DETECTION

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This document has been prepared for the purpose of providing guidance on the selection and use of portable volatile organic compound analyzers for monitoring process leaks. Specifically the types of volatile organic compound analyzers capable of performing U.S. EPA Method 21 determinations are discussed. The principles of operation, advantages and limitations of the various devices have been discussed. Sections providing guidance on the operation of each of four types of volatile organic compound analyzers--photoionization, flame ionization, infrared, and catalytic combustion--are included in the document.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Various techniques are available for monitoring volatile organic compound emissions from process leaks (fugitive emissions). This document provides an overview of these techniques and presents technical information concerning the operation of the various types of volatile organic compound analyzers.

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ABSTRACT

This document has been prepared for the purpose of providing guidance on the selection and use of portable volatile organic compound analyzers for monitoring process leaks. Specifically the types of volatile organic compound analyzers capable of performing U.S. EPA Method 21 determinations are discussed. The principles of operation advantages and limitations of the various devices have been discussed. Sections providing guidance on the operation of each of four types of volatile organic compound analyzers--photoionization, flame ionization, infrared, and catalytic combustion--are included in the document.

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LIST OF ABBREVIATIONS

AID	--Analytical Instrument Development, Inc.
FID	--flame ionization detector
GC	--gas chromatograph(y)
HC(s)	--hydrocarbon(s)
IR	--infrared
NEC	--national electrical code
NDIR	--nondispersive infrared
PID	--photoionization detector
VOC	--volatile organic compound

SECTION 1

INTRODUCTION

Emission of volatile organic compounds into the atmosphere can result in ozone production. Since high ozone levels have damaging effects on the environment and adversely impacts human health, control of this pollutant is essential. In order to achieve the National Ambient Air Quality Standard for ozone, the Clean Air Act requires states to issue regulations limiting the amount of VOCs which can be emitted from various sources.

While some VOC emissions are from classical point sources (e.g., stacks, automobiles), a large proportion of VOCs enter the atmosphere as fugitive emissions (leaks in valves, pumping systems, flanges, seals, and other types of process equipment). Consequently, detection and control of such fugitive emissions is important to the overall reduction of VOC emissions.

Fugitive VOC emissions are subject to Federal regulation under the New Source Performance Standards as well as the National Emission Standards for Hazardous Air Pollutants. In addition, the U.S. Environmental Protection Agency (EPA) publishes Control Technique Guideline documents which serve as an information base concerning useful methods for controlling fugitive VOC emissions for specific industries. In many cases, the Control Technique Guidelines are used as a basis for state and local regulation of fugitive VOC emissions. A review of the exact requirements for VOC monitoring and control from the various regulations is beyond the scope of this document. Therefore, the reader should consult the literature (1,2) for more specific regulatory information.

Effective control of fugitive VOC emissions requires a practical method for determining the location of leaks and other sources of fugitive emissions. While several sampling and analysis methods are available for determining VOC emissions, most require sophisticated equipment, highly trained personnel, or extensive completion time. Recently EPA published a method, designated as Method 21, intended for use as a rapid screening procedure for VOC emission points (1). Method 21 is presented in Appendix A of this document.

Method 21 is highly flexible in that the user can select any type of monitoring device which meets the specifications and performance requirements discussed later in this document. However, the method gives very little guidance as to which type of analyzer is most suitable for particular monitoring situations. A few reports are available (3-6) which describe and/or evaluate various VOC analyzers.

The primary objective of this document is to present a detailed summary of the available VOC monitoring approaches and to provide guidance to users concerning the advantages, limitations, and performance characteristics of the available techniques. Manufacturers' literature and various reports have been used as background material for this document.

Section 2 of this document summarizes Method 21's performance requirements and specifications, and the limitations and performance characteristics of the various techniques. The remaining four sections provide guidance on the operation of the four major types of VOC analyzers, flame ionization (FID), photoionization (PID), infrared adsorption (IR), and catalytic combustion detectors. The prospective user should consult current users and manufacturers for more detailed information on specific commercial devices.

SECTION 2

SUMMARY OF AVAILABLE VOC ANALYZERS

METHOD 21 PERFORMANCE REQUIREMENTS AND SPECIFICATIONS

Method 21 lists several specifications and performance characteristics which VOC analyzers must meet in order to qualify for use. These requirements are listed below:

(a) The device must respond to those organic compounds processed at the facility.

(b) The analyzer shall be capable of detecting the leak definition concentration (often 10,000 ppmv) specified in the applicable regulation.

(c) The scale of the instrument meter shall be readable to ±5% of the specified leak definition concentration.

(d) The instrument shall be equipped with a pump so that a continuous sample is provided to the detector. The nominal sample flow rate shall be 0.5 to 3 l/min.

(e) The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code (NEC) by the National Fire Prevention Association.

(f) The instrument response factors for the individual compounds to be measured must be less than 10 (compared to the reference compound specified in the applicable regulation).

(g) The instrument response time must be ≤30 sec, using the instrument configuration used during testing.

(h) The calibration precision must be ≤10% of the calibration gas value (relative standard deviation of ≤10%).

Requirement (a) is related to requirement (f) in that only compounds yielding at least 1/10 the detector response of the reference compounds are considered to be detectable. This requirement will frequently determine which VOC analyzers are applicable for a given compound.

Requirement (b) refers to the instrument's sensitivity toward the reference compound (rather than the specific compound of interest). As discussed later, some VOC analyzers require dilution of the sample stream to allow such high levels to be within the calibration range of the instrument. Requirement (c) also refers to the sensitivity toward the reference compound and, in essence, states that the detector shall respond to the reference compound on a level of 0.05 times the leak definition concentration.

Requirements (d) and (g) are also interrelated. The requirement for a continuous sample flow results from the need to decrease instrument response time to ensure that a leak can be observe after a short sampling interval. A continuous air flow also helps to minimize accumulation of materials (through adsorption or condensation) in the sample line. The response time is defined as the time required for the instrument to achieve 90% of the final reading when switched rapidly from zero gas (<10 ppmv of VOC) to the calibration gas (at the leak definition concentration).

Requirement (e), while not eliminating generic types of VOC analyzers, may require the use of certain models of VOC analyzers within each generic type since not all such devices may have met the NEC certification requirements.

The requirements listed above place certain restrictions on the types of VOC analyzers which can be used for specific applications. For example, stain tube detection systems will generally fail to meet the calibration precision requirement. The most useful VOC analyzers which may be capable of meeting the requirements of Method 21 employ:

- Flame ionization,
- Photoionization,
- Infrared adsorption, or
- Catalytic combustion.

However, not all commercial devices within the categories will meet Method 21 specifications and the user must therefore exercise caution in selecting a particular device. The principles of operation and performance characteristics of these four major types of VOC analyzers are discussed below.

PRINCIPLES OF OPERATION FOR SELECTED TYPES OF VOC ANALYZERS

Flame Ionization Detector

Flame ionization detectors (FIDs) are widely used for detecting organic compounds because of the relatively uniform response from compound to compound. A simplified diagram of an FID is shown in Figure 1. In the FID the sample stream is introduced into a hydrogen flame. Upon combustion in the flame organic compounds produce ions which are collected at an electrode and the resultant current flow is measured with an electrometer.

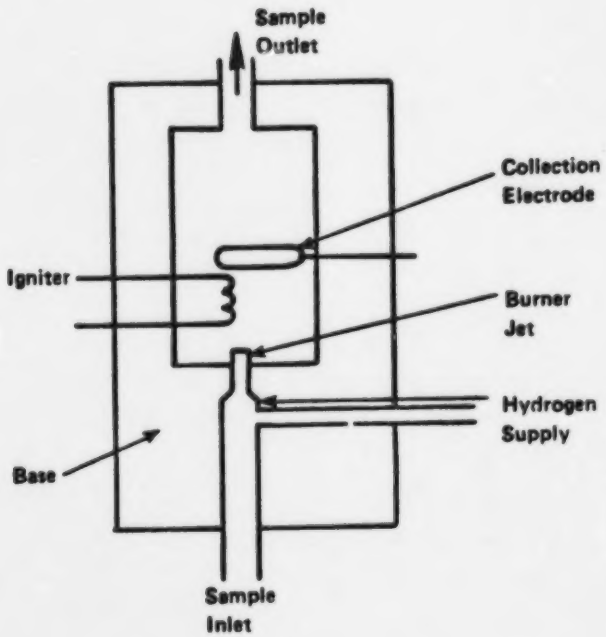

Figure 1. Flame ionization detector.

When the FID is used as a gas chromatography (GC) detector, separate air and sample streams are delivered to the detector whereas the stand-alone VOC monitors employ the sample stream as the air supply as well. This design difference affects the response characteristics of the detector to some extent. While the GC/FID system yields a response based on carbon weight the stand-alone FID responds more nearly on a molar basis. The reasons for this response difference are not clear; nevertheless, the operator of such instruments should be aware of this difference for the compounds of interest. In general, compounds containing elements other than carbon and hydrogen will give a reduced response relative to hydrocarbons (HCs). Response factors relative to methane for a variety of organic compounds on a portable FID system are provided in Appendix B.

Photoionization Detector

The photoionization detector (PID) system's operation, diagrammed in Figure 2, is similar to that of the FID except that ions are produced by an ultraviolet radiation source rather than a flame. Since the ionization potentials of organic compounds vary over a wide range, PIDs necessarily respond quite differently to the various compounds.

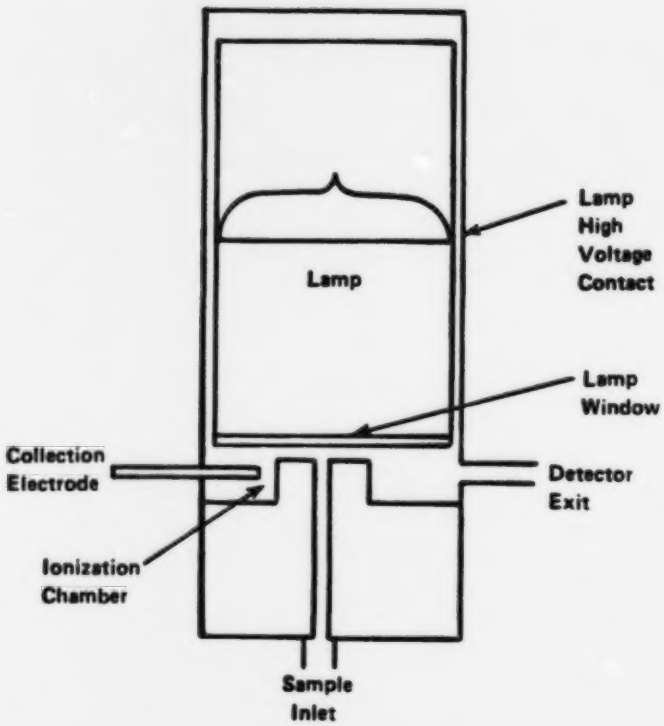

Figure 2. Photoionization detector.

Lamps of various energies (from 9 to 11 eV) are available and the choice of lamp energy greatly affects the response factors for various compounds. Only compounds with ionization potentials less than or equal to the lamp energy will be readily detected. Appendix C provides a list of ionization potentials for various compounds. In general, compounds having ionization potentials greater than 12 eV will not be readily detected by PID analyzers. A useful discussion of the use of PID and FID portable VOC analyzers is provided in a recent article (6). Response factors for a number of VOCs have been determined using a portable PID monitor (5).

Catalytic Combustion Detectors

A schematic diagram of the catalytic combustion detector is shown in Figure 3. This system uses a dual "hot-wire" cell in which one of the wires is coated with a catalyst to promote oxidation (combustion) of organic compounds present in the sample stream. The heat released during the combustion process results in a resistance change in the coated wire compared to the reference wire, and this imbalance produces a signal which is related to the VOC concentration. This detector responds to compounds in a fashion similar to the FID (i.e., highly oxygenated or chlorinated materials such as

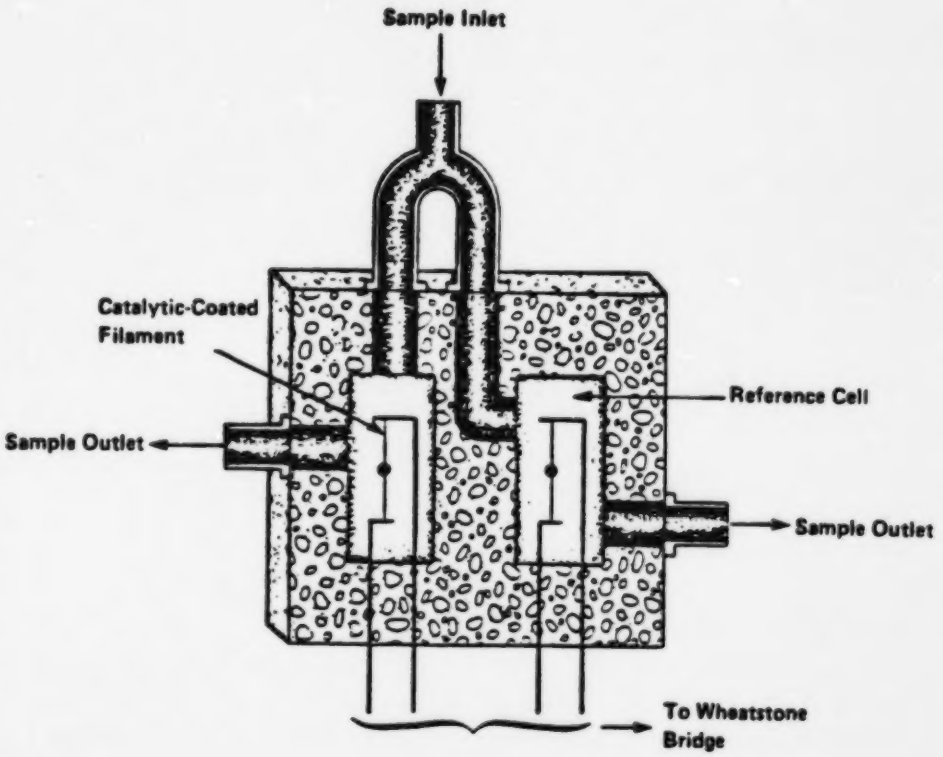

Figure 3. Catalytic combustion detector.

formaldehyde or carbon tetrachloride are less readily detected). Response factors for various compounds using a portable catalytic combustion unit are available in Appendix B.

Infrared Adsorption

Two types of infrared (IR) analyzers, nondispersive and dispersive, are available. In the nondispersive IR (NDIR) technique, IR radiation is directed through a reference cell as well as a sample cell. The sealed reference cell is filled with an inert, nonadsorbing gas such as nitrogen. The sample cell receives a continuous flow of sample gas. The detector consists of a double chamber filled with the compound of interest or a similar compound and an impermeable diaphragm separates the two halves of the cell. When the compound of interest is present in the sample cell, the incident radiation on one half of the detector decreases, resulting in movement of the diaphragm which is coupled to a capacitor. A detection signal results.

The other type of IR detector involves a direct adsorbance measurement at a particular wavelength selected by a filter or grating monochrometer. A simplified diagram of such a device is shown in Figure 4. This form of IR is generally more versatile than the nondispersive infrared technique and therefore the latter will not be discussed further in this document. A recent report describes the use of a portable IR system for detecting several VOCs and lists response factors (5).

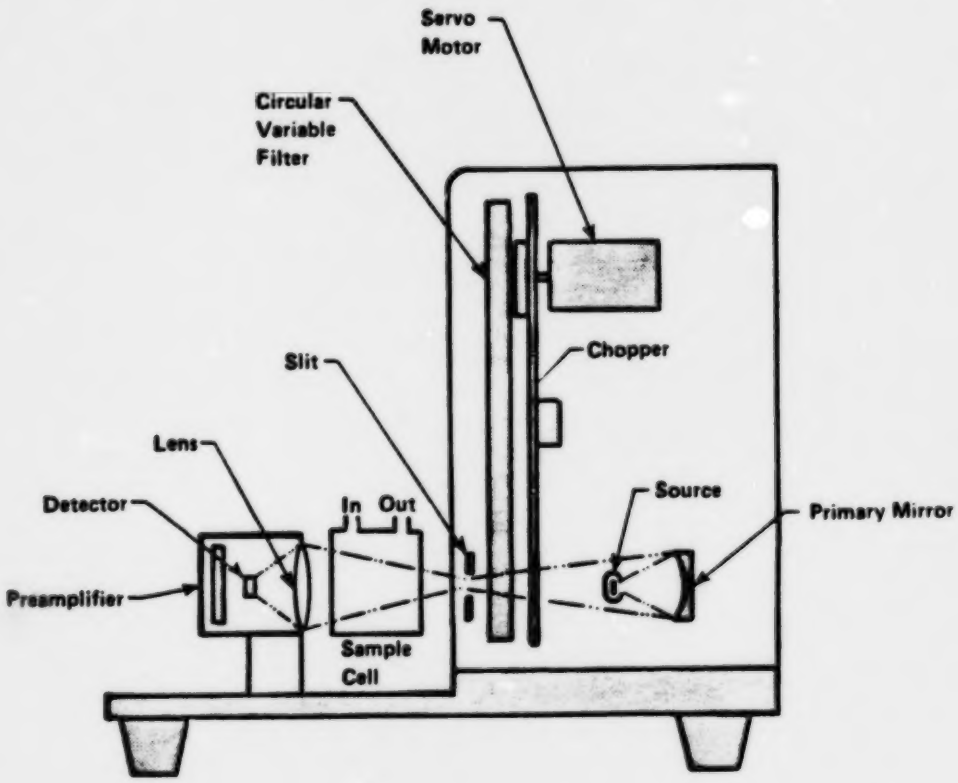

Figure 4. Dispersive infrared detector.

COMPARISON OF PERFORMANCE CHARACTERISTICS, ADVANTAGES, AND LIMITATIONS OF VOC MONITORING TECHNIQUES

This portion of the document addresses the inherent characteristics of the four major types of VOC analyzers and also lists commercially available detector models within each category. Table 1 presents a comparison of the four major types of VOC analyzers. Table 2 provides a representative list of commercially available instruments. This list is not comprehensive and in some cases the information available from manufacturing literature or other sources (3) may no longer be accurate. A more comprehensive list available in the literature (3) as well as recent manufacturers' literature and/or current users should be consulted when considering the purchase of a VOC analyzer.

As shown in Table 1, the four major types of VOC analyzers do not differ greatly in terms of response time or precision. However, the response time for catalytical combustion devices is somewhat slower than for the other devices, which can be a consideration if a large number of points are to be surveyed. Calibration accuracy is similar for the various instruments. However, one must recognize that the accuracy for a given compound may be much poorer than the value listed in Table 1 due to response differences between the calibration compound and the compound of interest.

Costs for the different types of VOC analyzers vary over a wide range although in general the catalytic combustion devices are least expensive, the IR devices are the most expensive, and the PIDs and FIDs have intermediate costs.

The detection range for the various analyzers is controlled by several factors including instrument configuration, pumping flow rate, and electrometer gain. Consequently, each analyzer is capable of spanning a wide range of concentrations. In general, the catalytic combustion units are least sensitive and certain commercial devices may not meet the sensitivity requirements of Method 21. In addition, several of these devices do not include a continuous sampling pump as required by Method 21. The other types of analyzers generally have adequate sensitivity. However, the PID units require a sample dilution system to achieve an upper operating range of 10,000 ppmv. This aspect of the PID analyzers is discussed in a recent report (5). Hopefully future improvements in dilution systems will make the PID systems more useful.

The major differences between the various types of VOC analyzers are the types of compounds which are detected and the degree of variation in response between compounds. As shown in Table 1, the FID systems readily detect all types of HCs and have approximately the same sensitivity for the various HCs. However, the FID response is decreased by the presence of elements other than carbon and hydrogen and is especially poor for halogenated and heavily oxygenated compounds.

TABLE 1. PERFORMANCE COMPARISON OF FOUR MAJOR TYPES OF VOC ANALYZERS

		FID	PID	Catalytic Combustion	IR
1.	Well detected VOC classes	Aliphatic olefinic, and aromatic HCs	Aromatic and olefinic HCs, chlorinated compounds	Similar to FID	HCs
2.	Poorly detected VOC classes	Highly oxygenated or halogenated compounds. Sulfur, nitrogen, phosphorus-containing compounds also give reduced response	Aliphatic HCs	Similar to FID	Highly dependent on IR adsorption spectrum. Water vapor will interfere with certain compounds.
3.	Typical calibration compound	Methane, propane	Benzene, butadiene	Methane, propane	Compound of interest or very similar compound
4.	Typical detection range (ppmv)	1 to 10,000	1 to 2,000 or 10 to 20,000 (with dilution)	Several ranges available from 10 ppm up to lower explosion limit	1 to 10,000. (Highly dependent on specific compound)
5.	Typical calibration accuracy (%)	2 to 10	5 to 10	2 to 10	2 to 10
6.	Typical calibration precision (%)	2 to 5	2 to 5	2 to 5	2 to 5
7.	Typical response time (sec)	5 to 10	5 to 10	5 to 20	5 to 100
8.	Approximate cost	$2500 to $5000	$4000 to $5000	$300 to $2000	$4000 to $7000
9.	Major advantages	a) Uniform response for most HCs b) Some response obtained for almost all organic compounds	a) Detects oxygenated and chlorinated compounds not detected by FID b) No external gas supply required	a) Low cost b) Relatively uniform response for most HCs c) No external gas supply required	a) Qualitative information may be obtained b) No external gas supply required
10.	Major limitations	a) Poor response for highly oxygenated or chlorinated compounds b) External gas supply (hydrogen) required	a) Does not respond to aliphatic HCs b) Detection of high levels may require dilution of the sample stream c) Unsuitable for refinery applications	a) Poor response for highly oxygenated or chlorinated compounds b) Not as sensitive as the other techniques	a) Water vapor and other atmospheric constituents may interfere b) Sensitivity highly dependent on the specific compound of interest c) Expensive d) Unsuitable for refinery applications

TABLE 2. COMMERCIALLY AVAILABLE PORTABLE VOC ANALYZERS[a]

Manufacturer	Model Number	Weight (lbs)	Approximate Cost ($)	Detection Range (ppmv)	Sensitivity (ppmv)	Calibration Accuracy (%)	Calibration Accuracy (%)	Response Time (sec)	Nominal Sampling Rate (</min)	Comments
FID										
Analytical Instrument Development, Inc. (AID) Avondale, PA	712	14	$4,600	1 to 2000 or 10 to 20,000	0.1 (as methane)	--	--	5	1.5	
Foxboro Analytical S. Norwalk, CT	OVA-108	12	$5,400	0 to 10,000	0.5 (as methane)	±2	2	2	2.0	GC available optional
FID										
AID Avondale, PA	585	8.2	$4,200	0 to 10,000	1 (as benzene)	--	--	9	0.05	10.0 and 11.8 eV available lamps
HNU Systems Newton Upper Falls, MA	PI-101	12	$4,000	0 to 2000	1 (as benzene)	--	--	5	0.5	9.5, 10.2, and 11.7 eV available lamps
Catalytic combustion										
Bacharach Instrument Co., Pittsburgh, PA	TLV Sniffer (0023-7356)	5	$1,200	0 to 50,000	2 (as methane)	±3	3	--	2	
Biomarine Industries Inc., Rexnard Electronic Products, Malvern, PA	901	3	$950	0 to 100% LEL[b]	--	--	--	5	--	Does not include sampling pump as required in Method 21.
Gas Tech, Inc. Mountain View, CA	1238	8	$850	0 to 100% LEL or 0 to 500 ppm	--	±5	2	4	--	Does not include sampling pump as required in Method 21.
Mine Safety Appliances Co., Pittsburgh, PA	100	8	$8,000	0 to 100% LEL	--	--	--	5	--	Does not include sampling pump as required in Method 21.
Infrared devices (dispersive)										
Foxboro Analytical, S. Norwalk, CT	Miran-1A	32	$7,000	ppm-% level	1 (highly dependent on compound of interest)	±2	3-4	selectable 1 to 40	--	

(a) This list is not comprehensive. Available information may no longer be accurate in certain cases.
(b) Lower explosion limit.

PID analyzers respond well to many of the compounds which are poorly detected by FID (e.g., oxygenated and halogenated compounds). Aromatic and olefinic HCs are also readily detected. However, PIDs give poor response for aliphatic HCs. An additional disadvantage of the PID analyzers is the wide variation in response from compound to compound within a class, due to differences in ionization potential (Appendix C). This problem is less severe when the highest energy lamps (e.g., 11.8 eV) are employed but is still significant in many cases.

The catalytic combustion detectors respond to compounds in a manner similar to the FID but with poorer overall sensitivity and considerably greater response variation between compounds. Response factor data for both the FID and catalytic combustion devices are presented in Appendix B (6). These data as well as the ionization potential data in Appendix C should be consulted when determining which type of analyzer is most suitable for a given application.

The IR devices are more complex with regard to applicable compounds and detection range. Unlike the other three devices, IR is subject to considerable interference from water vapor and other atmospheric constituents. Furthermore, large differences exist in spectral features and adsorption intensity between compound classes as well as between compounds within a class. Therefore, the use of IR should generally be limited to applications where only one or a few similar VOCs are expected to be present. IR devices have the advantage of providing qualitative information concerning compound identities by determining adsorption at several different wavelengths. The other devices yield such information only when used in conjunction with a GC.

Safety considerations are important when using all four types of VOC analyzers. Since all such devices have sampling pumps (as required by Method 21), an explosion hazard can exist if the instrument is not properly designed. The FID and catalytic combustion devices present additional potential hazards since a hydrogen flame is present in the former and combustion occurs during the detection process for the latter.

Method 21 requires VOC analyzers to be "intrinsically safe" for the environment in which they are used, as defined by NEC specification. Table 3 lists information concerning commercially available VOC analyzers which have been certified as intrinsically safe for certain industrial environments (3). Hazardous locations are divided into three classes: Class I, Class II, and Class III. Class I is the class of primary significance for VOC monitoring. Each class has two divisions (Division 1 or 2) according to the probability that a hazardous atmosphere will be present. Locations are also divided into seven groups depending on the type of hazardous material exposure. Groups A through D are flammable gases or vapors. Groups E, F, and G apply to combustible or conducting dusts and are of little significance in VOC monitoring. Class I, Division 1, Groups A, B, C, and D locations are those in which hazardous concentrations of flammable gases or vapors may exist under normal operating conditions.

TABLE 3. PORTABLE VOC DETECTOR INSTRUMENT CERTIFICATION[a]

Manufacturer	Model No.	Certification
AID, Avondale, PA	712	Intrinsically safe, Class I, Division 1, Groups A, B, C, &D
Bacharach Instrument Co., Pittsburgh, PA	TLV Sniffer	Intrinsically safe, Class I, Division I, Groups C & D, and Class I, Division 2, Groups A & B
Foxboro Analytical S. Norwalk, CT	OVA-108	Intrinsically safe, Class I Division 1, Groups A, B, C, & D
HNU Systems, Inc. Newton Upper Falls MA	PI-101	Intrinsically safe, Class I, Division 2, Groups A, B, C, & D

(a) This information has been obtained primarily from manufacturer's literature and has not been independently verified in all cases.

Class I, Division 2, Groups A, B, C, and D locations are those in which hazardous concentrations of flammables may exist only under unlikely conditions of operation. Instruments certified for use in Class I, Division 1, are safe in an explosive atmosphere whereas instruments certified for use in Class I, Division 2 are explosion proof but are not safe for use in an explosive atmosphere.

As shown in Table 3, no portable IR monitors are certified as "intrinsically safe" and hence this class of VOC analyzers is, at present, not suitable for Method 21 analyses. In fact, only a few VOC analyzers of any type meet this requirement.

Based on the above discussion, one must conclude that none of the four types of analyzers is best for all applications. Hence, one must carefully consider the types of compounds of interest in selecting a VOC analyzer. In general, the FID system is probably most useful in applications where petroleum HCs are of interest and is also useful for all but the most highly substituted (e.g., oxygenated, halogenated) compounds. The catalytic combustion system is also useful for these

applications but more variation in response between compounds will be observed. IR devices can be used for petroleum leak detection, but caution must be exercised since aliphatic and aromatic compounds are detected quite differently. Therefore, if the composition of the petroleum process stream is highly variable, IR devices probably should not be used. PID and IR devices generally will not be suitable for refinery applications (the most frequent anticipated use for Method 21) although these devices may be useful in certain areas of the synthetic organic chemicals industry.

The PID is useful for the highly substituted compounds such as oxygenated and halogenated materials. However, the PID is not as useful as the FID for petroleum leak detection because of the poor response for aliphatic HCs (compared to aromatics) and large compound-to-compound response variations for olefinic and aromatic compounds. The PID may be most useful in the certain areas of the synthetic organic chemicals industry in which halogenated and oxygenated solvents and similar materials are of concern.

SECTION 3

USE OF FLAME IONIZATION DETECTOR

The objective of this section and the following three sections is to discuss specific items relevant to the operation and maintenance of the four major types of VOC analyzers.

As shown in Table 3 and the literature (3), at least two portable FID analyzers are available which are potentially useful for performing Method 21 measurements. Although one of the units can be purchased with an optional GC column, in this document only the direct FID measurement will be described. Many of the operating details for the portable FID analyzers are identical to those for nonmethane organic carbon analyzers, except that the latter devices are not as portable. Therefore, one can refer to a recent Technical Assistance Document (8) for information not provided in detail in this document.

SYSTEM DESCRIPTION

A diagram of the FID itself is provided in Figure 1 and the principle of operation has been presented earlier in the document. The entire VOC analyzer, using an FID, is shown in Figure 5. The air sample is delivered to the flame housing by a sealed electric pump which generally operates from a 12-V battery supply. The sampling line consists of an intake probe, a filter to remove particles which would otherwise create a noisy baseline in the detector output, and a flowmeter which can be a rotometer or similar device.

The sample air stream is continuously delivered to the flame housing, mixed with hydrogen and combusted. The ions formed in the combustion process are collected at a collection electrode (usually held at a negative potential relative to the flame assembly which is held at ground potential). All gas inlet and outlet ports on the flame housing are usually fitted with sintered metal flame arrestors which prevent ignition of the atmosphere outside the housing, even when combustible gases are present.

The electrical current derived from ions arriving at the collection electrode is converted to a voltage using an electrometer and amplified. The resultant signal is fed to one or more output devices. Such output devices might include a stripchart recorder (if a long-term measurement is to be made), an analog or digital meter (either handheld or panel mounted), and/or an audible alarm.

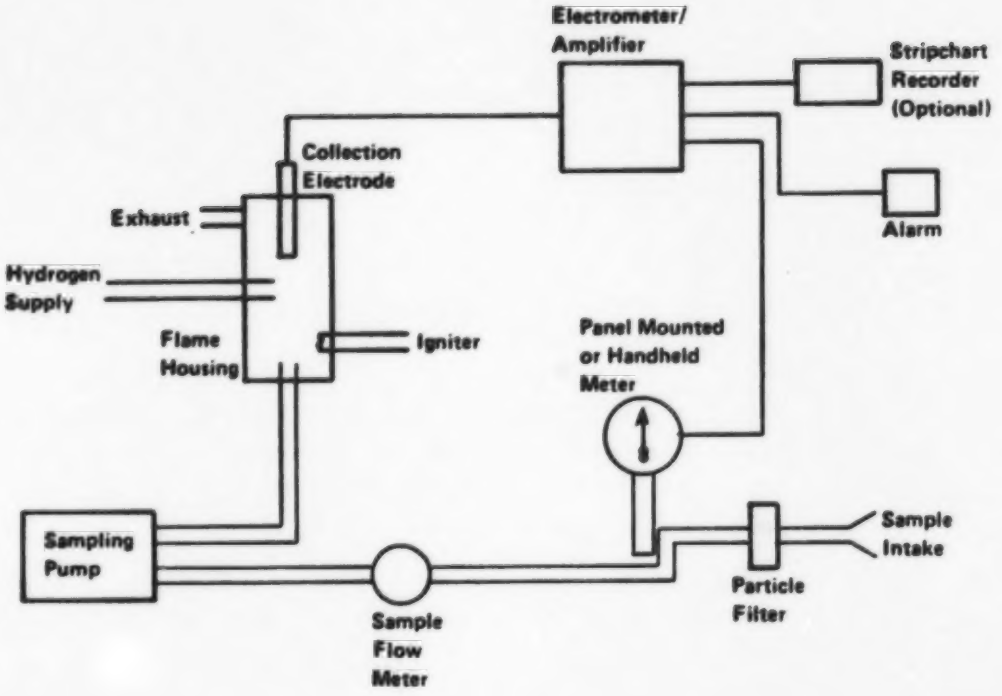

Figure 5. VOC analyzer using flame ionization detector.

SYSTEM OPERATION

Obviously, detailed operating procedures will vary from one device to another and cannot be fully described here. However, general guidelines for system operation are presented in Table 4 and discussed in the following portions of the document.

System Assembly and Startup

Prior to starting fuel flow or electronic components in the sample inlet, probe assembly should be visually inspected and installed. Caution must be exercised to insure that the airflow through the probe is not obstructed and that the probe is not heavily contaminated with oils or other organic compounds. The fuel supply and battery charge levels should be checked daily and replenished if necessary, according to the manufacturer's instructions. The installation of the flame arrestors (an important safety feature) should be checked and the electronics turned on and allowed

TABLE 4. GENERAL GUIDELINES FOR SYSTEM OPERATION USING AN FID ANALYZER

(1) Assembly/Startup

(a) Install probe assembly
(b) Check fuel supply
(c) Test power (battery) level
(d) Turn on electronics and set instrument zero
(e) Check installation of flame arrestors
(f) Start sampling pump and check sample flow/probe leackage
(g) Start fuel (hydrogen) flow, leak check, and ignite flame
(h) Null meter output using zero or background air. Set alarm levels, etc.
(i) Calibrate daily using reference compound specified in the regulations, or other suitable compound with known response factors.

(2) Operation

(a) Place sample probe at source to be measured and perform Individual Source Surveys in accordance with Section 4.3 of Method 21 (Appendix A).
(b) Periodically recheck zero setting using background or zero air supply.
(c) Avoid monitoring obvious leaks to avoid gross contamination of the instrument
(d) Periodically check flow rate and fuel supply and perform maintenance as required

(3) Shutdown

(a) Close fuel supply valve and tank valve.
(b) Shut down electronics except for sample pump.
(c) Wait 10 to 20 seconds and shut down sampling pump.

(4) Calibration

(a) Set instrument zero with flame off.
(b) Ignite flame and allow to stabilize as described for "Startup".
(c) Set zero using background (charcoal filtered) or zero air supply.
(d) Introduce known concentration of calibration compound near leak definition limit and observe reading. If necessary, adjust calibration knob to read known concentration and repeat zero and calibration determinations until further adjustment is not required.

(Continued)

TABLE 4. (Continued)

(5) Routine Maintenance

(a) Replenish fuel supply.
(b) Check/recharge batteries.
(c) Replace/clean particle filter
(d) Replace charcoal filter (background air inlet).
(e) Clean/replace flame arrestors.
(f) Leak-check flow system/gas supply lines.

(6) Quality Control/Performance Verification Procedures

(a) Check background (zero) air reading several times each day and after each high level measurement.
(b) Check calibration daily using calibration compound at level near the leak detection definition.
(c) Check air slow daily (observing instrument flowmeter) and whenever any maintenance is performed on the sampling flow system.
(d) Leak-check air flow system and fuel line daily (less frequently if no problems are observed historically).
(e) Check instrument response factor for regulated compound (relative to reference compound) before performing measurements. Literature values may be used, but are not recommended because of differences between instruments.
(f) Check calibration precision for three replicate determinations every three months or each use, whichever is longer.
(g) Check response time before performing leak detection measurements and whenever charges are made in the air flow, detector or electronic portions of the instrument.

to warm up for a 5 to 10 min period. The electronic zero of the instrument should then be set prior to starting any gas flow.

The sampling pump should then be started and the air flow measured. The probe assembly should be checked for leakage according to the manufacturer's instructions to insure that no sample dilution or contamination is present. The sample flow lines should be leak-checked both upstream and downstream of the pump. Since the downstream (detector) side of the pump operates under positive pressure this portion of the sample line can be leak-checked using a soap solution or similar fluid. To leak-check the sampling line upstream of the pump (which operates under a slight vacuum) one should cap the end of the probe and observe that the flow level is nearly zero. If a substantial flow is observed in this restricted condition, components of the sample line should be removed one by one and the restricted flow measurement repeated until the leak is identified.

Once a stable level of sample flow is achieved, the fuel flow can be initiated and the supply line checked for leaks using a soap solution or similar fluid. Once leak-free operation is verified, the flame can be ignited and the zero point of the detector set using a supply of uncontaminated air. For Method 21 applications, the zero air supply can be ambient (distant from potential VOC emission points) air in the vicinity of the plant being monitored, assuring the presence of VOC background levels of $\leq$10 ppmv. If the background air is more heavily contaminated a small cylinder of uncontaminated air may be carried for zeroing the instrument or the local ambient air can be drawn into the instrument through a charcoal filter to remove VOCs (except for methane and other light HCs). However, if a charcoal filter is used it must be checked for contaminant breakthrough and replaced periodically, and the air flow should be measured with the charcoal filter in place to insure that no significant restriction of air flow occurs.

After zeroing the instrument the audio alarm level and other output parameters should be set and the instrument calibrated with the reference compound. Daily calibration of instrument response is not normally required. The calibration method is discussed at a later point in this document.

Operation

Method 21 (Appendix A) describes the mechanics of making a VOC determination which do not differ significantly from one analyzer to another. As shown in Table 4, the zero setting of the instrument should be checked periodically, especially after a high VOC level is encountered, to insure that instrument drift or sampling line contamination is not a problem. The analyzer should not be exposed to obvious process leaks since the extremely high VOC level could result in serious contamination of the instrument.

The operator should periodically check the fuel and battery levels, and sampling flow rate, and perform necessary maintenance.

Shutdown

As shown in Table 4, the sequence of instrument shutdown steps are to close the fuel supply valve and tank valve, turn off electronics except for the sample pump, and, after a brief period, shut off the sample pump. Under no condition should the sample pump be turned off before the fuel system because of the chance for explosion due to hydrogen leakage.

Calibration

Method 21 (Appendix A) describes calibration requirements. Generally, the instrument is calibrated with the reference compound specified in the appropriate regulation, although one may use another calibration compound provided that a response factor is either determined experimentally or provided in the literature. In general, one should avoid using response factors from the literature since differences may exist between the various commercially available detectors.

Before calibration the instrument should be zeroed, the electronics and flame should be stabilized, and the clean reading (background) adjusted to zero. The calibration compound, at a concentration level in air near (~ 80% of) the leak definition level, should be introduced into the instrument at the same sampling flow rate as that used for the actual sample analyses. Sample flow rate does affect instrument response. If the instrument response requires adjustment to read the correct value the background air reading should be rechecked and the calibration procedure repeated until no further adjustments are required.

Calibration standards are most convenient when supplied in a pressurized tank since such standards can be used for several months or longer. However, many compounds (except for methane and other light HCs) may condense in the pressurized cylinder at the high concentration of interest in Method 21. Therefore, alternate procedures for preparing gaseous standards may be necessary (e.g., for benzene and less volatile compounds). In general, the best method for preparing such standards is to fill a clean Teflon or Tedlar (Teflon and Tedlar are registered trademarks of E.I. Dupont de Nemours and Co., Wilmington, Delaware) bag with a known quantity (10 to 20 l) of clean air and to inject a known quantity of the compound of interest into the bag. The bag should be prepurged 2 to 3 times with clean air. This gas mixture should be allowed to equilibrate for 30 to 60 min and then connected to the sampling probe during instrument calibration through an appropriate valve installed in the bag. Tedlar bags with the appropriate fittings installed are available from various suppliers and the preparation of VOC standards is discussed in the literature (5). The bags should be purged several times with clean air immediately after use to minimize contamination of the bag. Since high levels of combustible compounds are used for calibration, safety is a considerable concern. All such activities (sample preparation and calibration) must be conducted in a well ventilated area free from explosive hazards (e.g., motors, electrical equipment, etc.).

Routine Maintenance

The items important for routine maintenance of FID analyzers are listed in Table 4. Most of these items do not require further discussion. All of the maintenance procedures should be performed at a location remote from any potential high level VOC source because of the possibility of explosion during maintenance. This consideration is especially important during instrument refueling and the manufacturer's instructions should be carefully reviewed prior to performing any maintenance or supply procedures.

Quality Control/Performance Verification Procedures

Quality control and performance verification procedures are specified in Method 21 and summarized in Table 4. Items requiring daily performance are:

- Background air measurement,
- Calibration with reference or suitable alternate compound, and
- Sample air flow observation.

The sample flow system should be leak-checked daily initially but less frequently if problems are not commonly observed. This leak-check procedure should be performed whenever components (e.g., particle filters) are removed for cleaning or replaced.

Items requiring less frequent attention are:

- Response time measurement,
- Calibration precision, and
- Response factor for regulated compounds.

The response time should be determined, as described in Method 21, initially and after any changes in the sample flow or electrical systems. An approximate response time should be observed for the daily calibration measurements and corrective action should be taken if major increases in response time are observed.

Calibration precision must be determined, as described in Method 21, every three months or prior to each use, whichever is longer.

Response factors (relative to the reference compound specified in the regulation) for the regulated compound as well as the calibration compound (if different from the reference compound) need only be determined initially, but should be rechecked whenever major modifications are made to the instrument.

Safety

Safety considerations are somewhat instrument-specific and the user should consult the manufacturer's literature for detailed information. The primary safety concern is the possibility of explosion. This concern is especially important for FID units which contain a hydrogen flame. Only VOC units which are certified as intrinsically safe for the particular facility being monitored are permitted to be used for Method 21 measurements. Table 3 lists VOC devices which have been certified and the locations for which they are permitted.

The flame housing for portable FIDs generally has flame arrestors which prevent propogation of a flame beyond the housing. The operator should check to be sure the arrestors are properly installed prior to initiation of fuel flow and must shut off fuel flow if the devices require cleaning or replacement.

Refueling, battery charging or replacement, and similar servicing and maintenance procedures should not be performed in an area where high VOC levels might be present. All such procedures should be done in strict accordance with manufacturer's instructions. Only replacement parts (pump motors, fuses, etc.) approved by the manufacturer may be installed in the analyzer.

SECTION 4

USE OF PORTABLE PHOTOIONIZATION DETECTORS

As shown in Table 2, only two portable PID analyzers are available and user manuals for both instruments have been consulted in preparing this section of the document.

SYSTEM DESCRIPTION

The PID cell is shown in Figure 2 and the principle of operation has been discussed earlier in this document. Figure 6 shows an entire VOC analyzer based on the PID. The high voltage supply required for the UV lamp as well as for polarization of the collection electrode is not shown. The operation of the PID system is similar to that of the FID system (shown in Figure 5) with several important differences.

Both commercially available PID devices are directly usable only up to a concentration of 2000 ppm. Therefore, dilution of the incoming air stream is required. The AID Model 585 is available with a dilution probe in which the dilution air is drawn through a charcoal filter to remove organic contaminants (other than methane). A dilution system for the HNU Model PI-101 is not described in the user's manual for the instrument, but such a device has been supplied as a prototype (5). Both systems are designed to provide a 10-fold dilution of the incoming air stream. The details of these systems are provided in the literature (5) and the systems are somewhat more complex than the one shown in Figure 6.

Neither PID unit has a sample flow indicator, as was the case for many of the FID units. Because they are nondestructive detection systems, the PID analyzers are less flow sensitive, but variations in flow can effect the VOC concentration of the incoming air. Therefore, a relatively constant flow is required. The user should occasionally check the incoming air flow using a nonrestrictive flow measuring device (e.g., rotometer or wet test meter). The availability of a rotometer or similar device is important for periodically leak-checking the probe assembly as well.

The choice of lamp energy is an important parameter for PID detection. In most VOC applications the higher energy lamps (e.g., 11.8 eV) are most useful since this will insure that most organic compounds (other than short chain aliphatic HCs) are detected. However, the use of a high energy lamp is not necessary for VOCs which have low ionization potentials (see Appendix C). The AID instrument has both 10.0 and 11.8 eV lamps available and the HNU instrument has 9.5, 10.2, 10.9 and 11.7 eV lamps available.

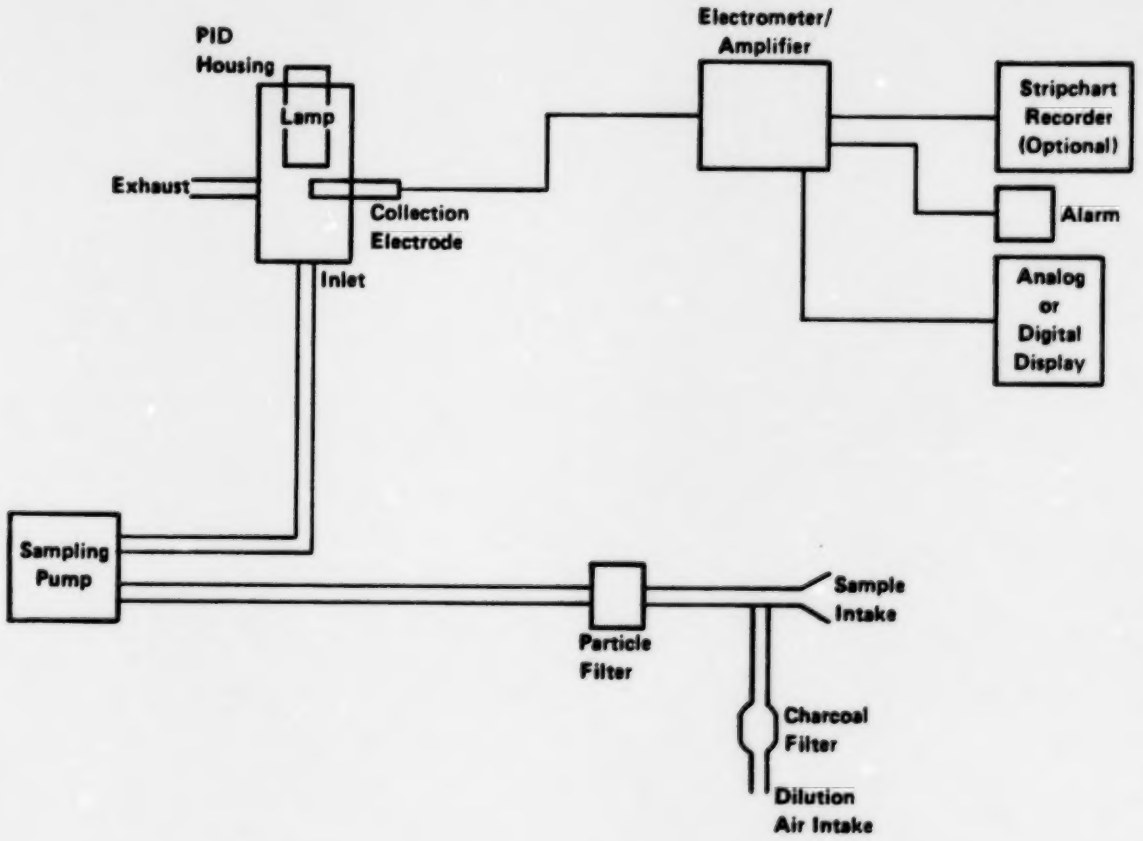

Figure 6. VOC analyzer using photoionization detector.

SYSTEM ASSEMBLY AND STARTUP

As shown in Table 5, the sample probe must be assembled and leak-checked prior to performing calibrations or source measurements. Caution must be exercised to insure that the sample flow is not obstructed and the probe is not contaminated with oils or other organic compounds. The HNU instrument's probe also contains the detector cell and the manufacturer's instructions should be carefully reviewed prior to performing any maintenance or adjustments on the probe assembly.

Although both available PIDs require the use of sample dilution assemblies as part of the sampling line, the exact design of these probes is not discussed in the manufacturer's literature available at this time. Furthermore, the probe configuration is likely to be modified and improved over the next several years. Therefore, the user should discuss the dilution probe design with the manufacturer to obtain current operating instructions prior to purchasing or using a PID unit for Method 21 applications.

After starting the electronics and pumping (fan) systems the sampling line should be leak-checked and the sample flow determined in a manner similar to that described for the FID system. Unfortunately, neither PID unit contains a flow indicator and therefore the operator must provide a nonrestrictive flow measuring device such as a rotometer or wet test meter. Because such equipment is not always readily available this measurement need not be performed daily, unless significant flow rate fluctuations are frequently observed. Although the manufacturer's instrument manuals state that the instrument response is not affected by variations in flowrate, such variations can cause a significant change in the inlet VOC concentration, depending on the type of fitting and the VOC leakage rate.

Once leak-free operation is achieved the instrument (electronic) zero should be set. The HNU system is placed in the standby position to adjust instrument zero whereas the AID system is zeroed with the input lines shorted using a jumper wire. The instrument is then placed in the "operate" mode and the output is zeroed using background air (<10 ppmv VOC). As for the other VOC devices, background air can be ambient air near the facility to be monitored (removed from any potential VOC sources), a cylinder supply of pure air, or ambient air drawn through a charcoal filter to remove organics. As discussed earlier, one should periodically replace any charcoal filter used since organic contaminants will eventually "break through" the sample flow with the charcoal. After the zero levels are set the instrument should be calibrated as described later in this section of the document.

Operation

The mechanics of performing a VOC determination are described in Method 21 (Appendix A) and do not differ significantly from one analyzer to another. As shown in Table 5, the zero setting of the instrument should be checked periodically, especially after a high VOC level is encountered, to ensure that contamination of the sampling line or instrument drift is not a problem. One should avoid exposing the analyzer to obvious process

TABLE 5. GENERAL GUIDELINES FOR SYSTEM OPERATION USING A PID ANALYZER

(1) Assembly/Startup

(a) Install probe assembly.
(b) Test power (battery) level.
(c) Turn on electronics and visually observe lamp to be operational.
(d) Leak-check sample line.
(e) Set electronic zero and alarm levels.
(f) Set zero using background (<10 ppm VOC) air.
(g) Calibrate using reference, or other suitable calibration compound at a concentration approximately 80% of the leak detection definition.

(2) Operation

(a) Place sample probe at source to be measured and perform Individual Source Surveys as described in Section 4.3 of Method 21 (Appendix A).
(b) Periodically recheck zero setting using background (zero) air.
(c) Avoid direct measurement of obvious leaks to avoid gross contamination of the instrument.
(d) Periodically check battery level and visually confirm lamp operation.

(3) Shutdown

(a) Place instrument in standby position.
(b) Shut off electronics.

(4) Calibration

(a) Set electronic zero.
(b) Set zero using background (zero) air.
(c) Introduce known concentration of calibration compound representing approximately 80% of the leak definition. If necessary, adjust calibration control to read known concentration. Repeat zero and calibration measurements until further adjustment is not necessary.

(5) Routine Maintenance

(a) Charge or replace batteries
(b) Replace/clean particle filter.
(c) Replace charcoal filter (dilution system).
(d) Replace/clean lamp cell window.
(e) Replace lamp.
(f) Leak-check sample flow system.

(Continued)

TABLE 5. (Continued)

(6) Quality Control/Performance Verification Procedures
(a) Check background (zero) air reading several times each day and after each high level measurement.
(b) Check calibration daily using calibration compound at level near the leak detection definition.
(c) Check air flow periodically, especially whenever any maintenance is performed on the sample flow system.
(d) Check instrument response factor for regulated compounds (relative to reference compound) before performing measurements. Literature values may be used, but are not generally recommended because of differences between instruments.
(e) Check calibration precision for three replicate determinations every three months or after each use, whichever is longer.
(f) Check response time before performing leak detection measurements and whenever changes are made in the air flow, detection or electronic portions of the instrument.

leaks since the extremely high VOC level could result in serious contamination of the instrument.

The operator should periodically check the power (battery level) and visually observed lamp operation, using the observation ports provided on the instrument.

Shutdown

PID shutdown procedures involve placing the instrument in the standby mode and turning off the electronic system.

Calibration

The PID's calibration requirements are essentially the same as those for the FID and the reader is directed to the calibration portion of Section 3 for detailed information. The PID response may be significantly different from one lamp to the next and therefore calibration is necessary each time the lamp is replaced. Calibration is also necessary whenever the detector cell is cleaned or otherwise serviced.

Since both PID units contain dilution systems, calibration may be required more frequently than for FID analyzers because of the presence of this additional source of variability.

Routine Maintenance

Routine maintenance procedures are listed in Table 5 and do not require much elaboration. Periodically, replacement/recharging of batteries, cleaning/replacement of particle filters, replacement of charcoal filters, and leak-checking the sample flow system are required. In addition, replacement of the PID lamp (every few hundred hours of operation) and cleaning of the cell (lamp) window every few weeks are necessary maintenance procedures.

Quality Control/Performance Verification Procedures

The procedures are identical to those for the FID and the reader is directed to the corresponding portion of Section 3 for further information.

Safety

Safety concerns for the PID analyzers are somewhat less critical than for FID since no open flame or fuel source is present. However, the electrical system has the potential for creating sparks which can initiate an explosion if caution is not exercised. As with FID units, any maintenance or repair work on a PID analyzer must be performed at a point remote from potential sources of VOC contamination. All such procedures should be done in strict accordance with manufacturer's instructions and only approved replacement parts (lamps, fan motors, fuses, etc.) may be installed in the analyzer.

SECTION 5

USE OF CATALYTIC COMBUSTION ANALYZERS

As shown in Table 2 and the literature (3), numerous portable catalytic combustion analyzers are potentially useful for performing Method 21 measurements. Because of the large number of such devices this section can be viewed only as generalized information and the reader should carefully review specific manufacturer's instructions before operating any particular device.

SYSTEM DESCRIPTION

With the exception of the detector cell and electronic measurement system, the catalytic combustion VOC analyzers are similar to the FID analyzers diagrammed in Figure 5. The cell configuration of the catalytic combustion device is shown in Figure 3 and the principle of operation has been previously discussed.

The sample pumping system for catalytic combustion devices is generally very similar to that shown in Figure 5 for the FID unit. The detector cell, shown in Figure 3, consists of measurement (catalytic filament) and reference (uncoated filament) compartments each of which received one-half of the total sample flow. The electronic measurement device is a Wheatstone bridge. As in the FID, the catalytic combustion cell has flame arrestors at all inlet and outlet points to prevent flame propagation outside the cell. The output display devices are generally the same as the one shown in Figure 5. Many devices display output calibrated as a percentage of the lower explosion limit. Therefore, one must determine the relationship between the lower explosion limit scale and component concentration (ppmv) for the VOC component of interest when performing Method 21 measurements.

In general, the catalytic combustion devices are designed for operation in air and will not function properly if large amounts of steam or other components are present or when an oxygen level of 25% or greater is present.

SYSTEM OPERATION

Obviously detailed operating procedures will vary from one device to another and cannot be fully described here. However, general guidelines for system operation are presented in Table 6 and discussed in the following portions of the document.

TABLE 6. GENERAL GUIDELINES FOR SYSTEM OPERATION USING A CATALYTIC COMBUSTION ANALYZER

(1) Assembly/Startup

(a) Install probe assembly.
(b) Test power (battery) level.
(c) Check installation of flame arrestors.
(d) Turn on electronics and allow a 5 to 10 minute warm-up period.
(e) Null meter output using zero or background air. Set alarm levels, etc.
(f) Calibrate daily using reference compound specified in the regulations, or other suitable compound for which the response factor is known.

(2) Operation

(a) Place sample probe at source to be measured and perform Individual Source Surveys in accordance with Section 4.3 of Method 21 (Appendix A).
(b) Periodically recheck zero setting using background or zero air supply.
(c) Avoid monitoring obvious leaks to avoid gross contamination of the instrument.
(d) Periodically check flow rate and perform maintenance as required.

(3) Shutdown

(a) Shut down electronics except for sample pump.
(b) Wait 10 to 20 sec and shut down sample pump

(4) Calibration

(a) Set instrument zero.
(b) Set zero using background (charcoal filtered) or clean air supply.
(c) Introduce known concentration of calibration compound near (~80% of) leak definition limit and observe reading. If necessary, adjust calibration knob to read known concentration and repeat zero and calibration determinations until further adjustment is not required.

(5) Routine Maintenance

(a) Replace filaments.
(b) Check/recharge batteries.
(c) Replace/clean particle filter.
(d) Replace charcoal filter (background air inlet).
(e) Clean/replace flame arrestor.
(f) Leak-check sample flow system.

(Continued)

TABLE 6. (Continued)

(6) Quality Control/Performance Verification Procedures

(a) Check background (zero) air reading several times each day and after each high level measurement.
(b) Check calibration daily using calibration compound at level near the leak detection definition.
(c) Check air flow daily (observing instrument flowmeter) and whenever any maintenance is performed on the sample flow system.
(d) Leak-check air flow system daily (less frequently if no problems are observed historically).
(e) Check instrument response factor for regulated compound (relative to reference compound) before performing measurements. Literature values may be used, but are not recommended because of differences between instruments.
(f) Check calibration precision for three replicate determinations every three months or each use, whichever is longer.
(g) Check response time before performing leak detection measurements and whenever changes are made in the air flow, detector or electronic portions of the instrument.

System Assembly and Startup

Prior to activating the electronics the sample inlet probe assembly should be visually inspected and installed. Caution must be exercised to insure that the air flow through the probe is not obstructed and that the probe is not heavily contaminated with oils or other organic compounds. The battery charge levels should be checked daily and recharged if necessary, according to the manufacturer's instructions. The installation of the flame arrestors (an important safety feature) should be checked and the electronics turned on and allowed to warm up for a 5 to 10 min period. In most instruments sample flow occurs as soon as the electronics are turned on and therefore, the zero point must be set with a continuous flow of background air (<10 ppmv VOC).

Since the heated filaments require a continuous flow of air the instrument should not be leak-checked using the restriction technique described for FID analyzers. If leakage on the vacuum side of the pump is suspected, a VOC compound to which the device is sensitive (e.g., propane) can be sprayed near the points where leakage might occur and the instrument's response will indicate the degree of leakage. Manufacturer's instructions should be consulted with regard to checking sample flow and/or leakage in the flow assembly.

Once leak-free operation is verified the zero point of the detector can be set using a supply of uncontaminated air. For Method 21 applications, the zero air supply can be ambient (distant from potential VOC emission points) air in the vicinity of the plant being monitored, assuming VOC background levels of 1 to 10 ppmv are present. If the background air is more heavily contaminated a small cylinder of uncontaminated air can be drawn into the instrument through a charcoal filter to remove VOCs (except for methane and other light HCs). However, if a charcoal filter is used it must be checked for breakthrough of contaminants and replaced periodically, and the air flow should be observed with the charcoal filter in place to insure that no significant restriction of air flow occurs.

After the instrument is zeroed, the audio alarm level and other output parameters should be set and the instrument calibrated with the reference compound, or suitable calibration compound. The calibration method is discussed at a later point in this document.

Operation

The mechanics of performing a VOC determination are described in Method 21 (Appendix A) and do not differ significantly from one analyzer to another. As shown in Table 6, the zero setting of the instrument should be checked periodically, especially after a high VOC level is encountered, to insure against contamination of the sampling line or instrument drift. One should avoid exposing the analyzer to obvious process leaks since the extremely high VOC level could result in serious contamination of the instrument.

The operator should periodically check the battery level and sample flow rate and perform maintenance as necessary.

Shutdown

Shutdown of the catalytic combustion devices simply involves turning off the electronics. If the sampling pump is not controlled by the same switch as the other electronic components, then the sample pump should be turned off last to prevent damage to the heated filaments.

Calibration

Calibration procedures for the catalytic combustion devices are essentially the same as those for the FID and the reader is directed toward the corresponding portion of Section 3.

Routine Maintenance

Routine maintenance items for the catalytic combustion systems are listed in Table 6 and do not require elaboration. All of the maintenance procedures should be performed at a location remote from any potential high level VOC sources because of the possibility for explosion during the maintenance activity. The user should carefully review the manufacturer's instructions before performing any maintenance procedures.

Quality Control/Performance Verification Procedures

These procedures, shown in Table 6, are identical to those previously described for FID and the reader is directed to the corresponding portion of Section 3.

Safety

Safety considerations for the catalytic combustion units are essentially the same as those for FID systems. These considerations are discussed in Section 3.

SECTION 6

USE OF INFRARED ANALYZERS

As shown in Table 3, dispersive IR analyzers are available from Foxboro Analytical. This section will focus on the use of this type of instrument, since NDIR devices are generally not versatile enough for use as VOC analyzers. However, NDIR systems may be of some use for a limited number of VOC monitoring applications where the operator is certain that only the VOC of interest is present. NDIR systems have been discussed in the literature (2,3) and will not be further discussed in this document.

SYSTEM DESCRIPTION

A diagram of the IR detector is shown in Figure 4 and the principle of operation has been previously discussed. Since only a single manufacturer (Foxboro) was identified, the following discussion is based primarily on literature available for one device, namely the Miran 80 detector. The potential applicability of this particular instrument has been discussed in the literature.

The IR analyzer simply consists of the detector (Figure 4) and a sample delivery system similar to that shown in Figure 5 for the FID. The sample delivery system consists of a pump, a 10 f sample line, and a particle filter. Since the detector is an optical system, removal of particles and condensed moisture from the system is extremely critical for proper operation.

The Miran Model 80 detector can perform adsorbance measurements in the 2.5 to 14.5 μm range using a filter wheel to select the wavelength. A built-in computer system allows rapid measurements to be performed at several different wavelengths. A variable pathlength mirror system is available to adjust the detection range. For performing measurements at levels of interest in Method 21 (500 to 10,000 ppmv) a pathlength of approximately 0.75 m was found to be suitable (5).

Unlike the FID, PID, and catalytic combustion units, the IR system is inherently selective and its selectivity is vastly affected by the choice of wavelength. Consequently, the system is more complex to use as a general VOC analyzer since different operating conditions are required for each type of compound.

In addition, major atmospheric constituents such as water and carbon dioxide can interfere in the analysis, depending on the analytical wavelength chosen. These features of the IR system must be kept in mind when using IR as a VOC monitoring device.

An important feature of the IR analyzer is the ability to obtain qualitative information concerning component identities by monitoring at several wavelengths. This feature is described in the manufacturer's literature and will not be discussed in detail here.

SYSTEM OPERATION

Guidelines for operating the IR instrument are provided in Table 7 and discussed below.

Assembly/Startup

The IR system is considerably more complex to use for VOC monitoring than the other types of analyzers because of the need to select appropriate conditions for each compound of interest. As with the other analyzers, the sample probe assembly should be installed and the battery level checked prior to turning on the electronic system. Installation of the particle filter is crucial since particulate matter can damage the detector cell. After starting the electronic system (which also activates the pump) a sufficient warmup period should be allowed to achieve a stable temperature within the detector cell. If the possibility for moisture condensation exists because of high humidity conditions, a clean, dry purge gas (air or nitrogen) should be passed through the cell during the warmup period since condensed moisture can damage the cell.

Prior to performing zero or calibration procedures, the analytical and reference wavelengths for each VOC of interest must be selected. This information is stored in the Miran 80's computer system and the user should consult the operator's manual for specific instructions on how this is accomplished.

The sample flow system should be leak-checked as described for FID devices. Since the Miran 80 does not have a built-in flow measuring device, the user must supply a rotometer or other nonrestrictive flow measuring device and appropriate fittings to perform this measurement. Although the flow rate does not directly affect the IR intensity, since the detector is nondestructive, flow rate changes can alter the VOC concentration entering the detector from the process leak.

The alignment of the optical system should be checked periodically as described in the operator's manual. The frequency with which alignment is required will depend on the usage conditions and must be based on user experience. Daily alignment should not be required although weekly or monthly alignment may be necessary.

TABLE 7. GENERAL GUIDELINES FOR SYSTEM OPERATION USING AN IR DETECTOR

(1) Assembly/Startup

(a) Install probe assembly.
(b) Check battery level.
(c) Turn on electronics and allow instrument to warm up for 10 to 15 min. Purge optical cell with clean, dry air or nitrogen if moisture condensation is a problem (i.e., high humidity situations).
(d) Select analytical and reference wavelengths for VOC of interest, based on reference spectra and potential interferences.
(e) Leak-check sample flow assembly.
(f) Check optical system alignment.
(g) Determine detector output for background (zero) air supply.
(h) Calibrate daily using reference compound specified in the regulation or suitable calibration compound with a known response factor.

(2) Operation

(a) Place sample probe at source to be measured and perform Individual Source Surveys in accordance with Section 4.3 of Method 21 (Appendix A).
(b) Periodically recheck zero setting using background or zero air supply.
(c) Avoid monitoring obvious leaks to avoid gross contamination of the instrument.
(d) Periodically check sample flow rate and perform required maintenance.
(e) Perform measurements at alternate wavelengths as appropriate to confirm identity of the monitored VOC.

(3) Shutdown

(a) Shut down electornics.

(4) Calibration

(a) Set zero using background (charcoal filtered) or zero air supply.
(b) Introduce known concentration of calibration compound near leak definition limit and observe reading. If necessary, adjust calibration output to read known concentration and repeat zero and calibration determinations until further adjustment is not required.
(c) Repeat process for each analytical wavelength of interest.

(Continued)

TABLE 7. (Continued)

(5) Routine Maintenance

(a) Flush/clean optical cell.
(b) Check/recharge batteries.
(c) Replace/clean particle filter.
(d) Replace charcoal filter (background air inlet), if applicable.
(e) Leak-check sample flow system.

(6) Quality Control/Performance Verification Procedures

(a) Check background (zero) air reading several times each day and after each high level measurement.
(b) Check calibration daily using calibration compound at level near the leak detection definition for each wavelength of interest
(c) Check air flow daily and whenever any maintenance is performed on the sample flow system.
(d) Leak-check air flow system daily (less frequently if no problems are observed historically.
(e) Check instrument response factor for regulated compound (relative to reference compound) before performing measurements. Literature values may be used, but are not recommended because of differences between instruments.
(f) Check calibration precision for three replicate determinations every three months or each use, whichever is longer.
(g) Check response time before performing leak detection measurements and whenever changes are made in the air flow, detector or electronic portions of the instrument.

Zeroing and calibration procedures are performed daily, or more frequently and are similar to those described for the other detectors, except that calibration at more than one wavelength may be necessary.

Operation

Operation of the IR monitor is essentially as described for the other detectors and the reader is directed to the corresponding portion of Section 3 for further discussion. User interaction with the Miran 80 computer system is described in the operator's manual and is not discussed in this document.

VOC determinations at each of several wavelengths will often be necessary, especially when a high level leak is encountered to confirm the identity of the VOC component and verify freedom from interferences (e.g., water vapor).

Shutdown

The shutdown procedure for the Miran 80 simply involves turning off the electronics.

Calibration

Calibration of the Miran 80 IR system is similar, in principle to that of the other detectors in terms of sources of clean air and methods for preparing gaseous standards. These considerations are discussed in the corresponding portion of Section 3. However, a few additional items must be considered for IR instrument calibration.

In particular, the choice of analytical and reference wavelengths for each VOC component is critical. One must consider potential interferences from inorganic gases (e.g., water vapor). In addition, if a mixture of VOCs is of interest one must consider potential spectral interferences between the components of the mixture. In such cases, measurement at several wavelengths is a requirement since the composition of the mixture may change with time or the component mixture emitted from the source may be different than the original mixture. Furthermore, since the IR analyzer uses the reference wavelength as a "zero adsorbance" point, this wavelength must not lie in an adsorptive region for any potential interferences, whose concentration may change with time.

Having selected appropriate analytical and reference wavelengths one must select an appropriate pathlength so that the VOC concentration of interest (the leak detection definition) will be within the linear range of the instrument. For Method 21 applications, a 0.75 meter pathlength has been found suitable (5) although this parameter will depend on the compound of interest and the wavelengths selected.

Routine Maintenance

The procedures shown in Table 7 generally do not require further elaboration. Cleaning and alignment of the optical cell are relatively delicate procedures and should be done with extreme care to avoid damaging the instrument.

Quality Control/Performance Verification Procedures

These procedures are essentially the same as those for FID and the reader is directed to the corresponding portion of Section 3 for further discussion.

Safety

Safety considerations are not particularly critical for the IR unit since flammable gas supplies, flames, etc., are not present. Normal precautions should be taken in that maintenance procedures (e.g., battery recharging) should not be performed in an area of potential VOC contamina-

tion. All such procedures should be done in strict accordance with manufacturer's instructions. Only replacement parts (pump motors, fuses, etc.) approved by the manufacturer may be installed in the analyzer.

REFERENCES

1. U.S. Environmental Protection Agency. Volatile Organic Compounds (VOC) Fugitive Emission Sources in the Synthetic Organic Chemicals Manufacturing Industry. Addition of Reference Method 21 to Appendix A. Federal Register, 48 (161): 37598-37602, August 18, 1983.

2. Course SI:417- Controlling VOC Emissions from Leaking Process Equipment - Student Guidebook, EPA 450/2-82-015, U.S. Environmental Protection Agency, Air Pollution Training Institute, Research Triangle Park, North Carolina, 1982. 86 pp.

3. Anastas, M. Y. and H. J. Belkap. Summary of Available Portable VOC Detection Instruments. EPA-340/1-80-010, U.S. Environmental Protection Agency, Washington D. C., 1980. 31 pp.

4. U.S. Environmental Protection Agency. Measurement of Volatile Organic Compounds. EPA-450/2-78-041, Research Triangle Park, North Carolina, 1979. 61 pp.

5. Menzies, K. T. and R. E. Fasano. Evaluation of Potential VOC Screening Instruments. EPA-600/7-82-063. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1982. 72 pp.

6. Brown, G. E., D. A. DuBose, W. R. Phillips, and G. E. Harris. Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Chemicals. EPA-600/52-81-002, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1981. 98 pp.

7. Sexton, F. W., R. M. Michie, F. F. McElroy, and V. L. Thompson. Technical Assistance Document for the Calibration and Operation of Automated Ambient Nonmethane Organic Compound Analyzers. EPA-600/4-81-015, U.S. Environmental Protection Agency, Research Triangle Park North Carolina, 1981. 105 pp.

8. Debbrecht, F. S. Comparison of Techniques for the Quantitation of Fugitive Emissions. Paper No. 82-66.6. In: Proceedings from Annual Meeting, Air Pollution Control Association, Pittsburgh, Pennsylvania, 1982.

9. DuBose, D. A. and G. E. Brown. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. EPA-600/2-81-051, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1981. 25 pp.

APPENDIX A

METHOD 21. DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile organic compound (VOC) leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.2 Principle. A portable instrument is used to detect VOC leaks from individual sources. The instrument detector typs is not specified, but it must meet the specifications and performance criteria contained in Section 3. A leak definition concentration based on a reference compound is specified in each applicable regulation. This procedure is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rates from individual sources.

2. Definitions

2.1 Leak Definition Concentration. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

2.2 Reference Compound. The VOC species selected as an instrument calibration basis for specification of the leak definition concentration (For example: If a leak definition concentration is 10,000 ppmv as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument calibrated with methane would be classified as a leak. In this example, the leak definition is 10,000 ppmv, and the reference compound is methane.)

2.3 Calibration Gas. The VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a concentration approximately equal to the leak definition concentration.

2.4 No Detectable Emission. The local VOC concentration at the surface of a leak source that indicates whether a VOC emission (leak) is present. Since background VOC concentrations may exist, and to account for instrument

drift and imperfect reproducibility, a difference between the source surface concentration and the local ambient concentration is determined. A difference based on meter readings of less than a concentration corresponding to the minimum readability specification indicates that a VOC emission (leak) is not present. (For example, if the leak definition in a regulation is 10,000 ppmv, then the allowable increase in surface concentration versus local ambient concentration would be 500 ppmv based on the instrument meter readings.)

2.5 Response Factor. The ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the application regulation.

2.6 Calibration Precision. The degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentrations.

2.7 Response Time. The time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90% of the corresponding final value is reached as displayed on the instrument readout meter.

3. Apparatus

3.1 Monitoring Instrument.

3.1.1 Specifications.

(a) The VOC instrument detector shall respond to the compounds being processed. Detector types which may meet this requirment include, but are not limited to, catalytic oxidation, flame ionization, infrared adsorption, and photoionization.

(b) The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

(c) The scale of the instrument meter shall be readable to ±5% of the specified leak definition concentration.

(d) The instrument shall be equipped with a pump so that a continuous sample is provided to the detector. The nominal sample flow rate shall be 1/2 to 3 liters per minute.

(e) The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the applicable U.S.A. standards (e.g., National Electrical Code by the National Fire Prevention Association).

3.1.2 Performance Criteria.

(a) The instrument response factors for the individual compounds to be measured must be less than 10.

(b) The instrument response time must be equal to or less than 30 seconds. The response time must be determined for the instrument configuration to be used during testing.

(c) The calibration precision must be equal to or less than 10% of the calibration gas value.

(d) The evaluation procedure for each parameter is given in Section 4.4.

3.1.3 Performance Evaluation Requirements.

(a) A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

(b) The calibration precision test must be completed prior to placing the analyzer into service, and at subsequent 3-month intervals or at the next use whichever is later.

(c) The response time test is required prior to placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required prior to further use.

3.2 Calibration Gases. The monitoring instrument is calibrated in terms of parts per million by volume (ppmv) of the reference compound specified in the applicable regulation. The calibration gases required for monitoring and instrument performance evaluation are a zero gas (air, <10 ppmv VOC) and a calibration gas in air mixture approximately equal to the leak definition specified in the regulation. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within ±2% accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life. Alternately, calibration gases may be prepared by the user according to any accepted gaseous standards preparation procedure that will yield a mixture accurate to within ±2%. Prepared standards must be replaced each day of use unless it can be demonstrated that degradation does not occur during storage.

Calibrations may be performed using a compound other than the reference compound if a conversion factor is determined for that alternative compound so that the resulting meter readings during source surveys can be converted to reference compound results.

4. Procedures

4.1 Pretest Preparations. Perform the instrument evaluation procedures given in Section 4.4 if the evaluation requirements of Section 3.1.3 have not been met.

4.2 Calibration Procedures. Assemble and start up the VOC analyzer according to the manufacturer's instructions. After the appropriate warm-up period and zero or internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value. (Note: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.)

4.3 Individual Source Surveys

4.3.1 Type I - Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

(a) Valves--The most common source of leaks from valves is at the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housing of multipart assembly at the surface of all interfaces where leaks could occur.

(b) Flanges and Other Connections--For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

(c) Pumps and Compressors--Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

(d) Pressure Relief Devices--The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

(e) Process Drains--For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

(f) Open-Ended Lines or Valves--Place the probe inlet at approximately the center of the opening to the atmosphere.

(g) Seal System Degassing Vents and Accumulator Vents--Place the probe inlet at approximately the center of the opening to the atmosphere.

(h) Access Door Seals--Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse

4.3.2 Type II - "No Detectable Emission". Determine the local ambient concentration around the source by moving the probe inlet randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration described in 4.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation.

For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

(a) Pump or Compressor Seals--If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described above.

(b) Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices--If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur prior to the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere prior to the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in this paragraph shall be used to determine if detectable emissions exist.

4.3.3 Alternative Screening Procedure. A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmsophere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of 4.3.1 or 4.3.2.

Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or a squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks, as applicable. If any bubbles are observed, the instrument techniques of 4.3.1 or 4.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

4.4 Instrument Evaluation Procedures. At the beginning of the instrument performance evaluation test, assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

4.4.1 Response Factor. Calibrate the instrument with the reference compound as specified in the applicable regulation. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration of approximately 80% of the applicable leak definition unless limited by volatility or explosivity. In these cases, prepare a standard at 90% of the saturation concentration, or 70% of the lower explosive limit, respectively. Introduce this mixture to the analyzer and record the observed meter reading. Introduce zero air until a stable reading is obtained. Make a total of three measurements by alternating between the known mixture and zero air. Calculate the response factor for each repetition and the average response factor.

Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in Section 5.

4.4.2 Calibration Precision. Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

4.4.3 Response Time. Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. Measure the time from switching to when 90% of the final stable reading is attained. Perform this test sequence three times and record the results. Calculate the average response time.

5. Bibliography

5.1 DuBose, D. A. and G. E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC, Publication No. EPA 600/2-81-051. September 1981.

5.2 Brown, G. E., et al. Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC, Publication No. EPA 600/2-81-022. May 1981.

5.3 DuBose, D. A., et al. Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC, Publication No. EPA 600/2-81-110. September 1981.

APPENDIX B

TYPICAL RESPONSE FACTORS RELATIVE TO METHANE AT 10,000 ppmv For FID AND CATALYTIC COMBUSTION VOC ANALYZERS

Compound Name	Response Factor[a]	
	FID	Catalytic Combustion
Acetic acid	1.64	15.60
Acetic anhydride	1.39	5.88
Acetone	0.80	1.22
Acetone cyanohydrin	3.51	21.00
Acetonitrile	0.95	1.18
Acetophenone	18.70	--
Acetyl chloride	2.04	2.72
Acetylene	0.39	--
Acrylic acid	4.59	--
Acrylonitrile	0.97	3.49
Allene	0.64	15.00
Allyl alcohol	0.96	--
Amyl alcohol,n-	0.75	2.14
Amylene	0.44	1.03
Anisole	0.92	3.91
Benzaldehyde	2.46	--
Benzene	0.29	1.07
Benzonitrile	2.99	--
Benzoyl chloride	22.10	--
Benzyl chloride	15.30	--
Bromobenzene	0.40	1.19
Butadiene, 1,3-	0.57	10.90
Butane, n-	0.50	0.63
Butanol, n-	1.44	4.11
Butanol, sec-	0.76	1.25
Butanol, tert	0.53	2.17
Butene, 1-	0.58	5.84
Butyl Acetate	0.66	1.38
Butyl Acrylate, n-	0.70	2.57
Butyl Ether, n-	2.60	3.58
Butyl Ether, Sec	0.35	1.15
Butylamine, n-	0.69	2.02
Butylamine, Sec-	0.70	1.56
Butylamine, Tert-	0.63	1.95
Butylbenzene, Tert-	1.32	--
Butyraldehyde n-	1.29	2.30
Butyric acid	0.80	6.53
Butyronitrile	0.52	1.47
Carbon Disulfide	--	3.92
Chloroacetaldehyde	9.10	5.07
Chlorobenzene	0.38	0.88
Chloroethane	5.38	3.90
Chloroform	9.28	--
Chlorophenol, 0-	4.58	18.30

Compound Name	Response Factor[a]	
	FID	Catalytic Combustion
Chloropropene, 1-	0.67	0.87
Chloropropene, 3-	0.80	1.24
Chlorotoluene, m-	0.48	0.91
Chlorotoluene, o-	0.48	1.06
Chlorotoluene, p-	0.58	1.17
Cresol, o-	0.96	4.36
Crotonaldehyde	1.25	--
Cumene	1.87	--
Cyclohexane	0.47	0.70
Cyclohexanol	0.85	--
Cyclohexanone	1.50	7.04
Cyclohexene	0.49	2.17
Cyclohexylamine	0.57	1.38
Decane	0.90	0.16
Diacetone alcohol	1.45	0.98
Diacetyl	1.54	3.28
Dichloro-1-propene, 2,3-	0.75	1.75
Dichlorobenzene, m-	0.65	2.36
Dichlorobenzene, o-	0.68	1.26
Dichloroethane, 1,1-	0.78	1.86
Dichloroethane, 1,2-	0.95	2.15
Dichloroethylene, CIS 1,2-	1.27	1.63
Dichloroethylene, trans 1,2	1.11	1.66
Dichloromethane	2.81	3.85
Dichloropropane, 1,2-	1.03	1.65
Diisobutylene	0.35	1.41
Dimethoxy ethane, 1,2-	1.22	1.52
Dimethylformamide, N, N-	4.19	5.29
Dimethylhydrazine 1,1-	1.03	2.70
Dimethylsulfoxide	0.07	8.45
Dioxane	1.48	1.31
Epichlorohydrin	1.69	2.03
Ethane	0.65	0.69
Ethanol	1.78	--
Ethoxy ethanol, 2-	1.55	1.82
Ethyl acetate	0.86	1.43
Ethyl acetoacetate	3.82	5.60
Ethyl acrylate	0.77	--
Ethyl chloroacetate	1.99	1.59
Ethyl ether	0.97	1.14
Ethylbenzene	0.73	4.74
Ethylene	0.71	1.58
Ethylene oxide	2.46	2.40
Ethylenediamine	1.73	3.26
Formic acid	14.20	--

Compound Name	Response Factor(a)	
	FID	Catalytic Combustion
Glycidol	6.88	5.66
Heptane	0.41	0.73
Hexane, n-	0.41	0.69
Hexene, 1-	0.49	4.69
Hydroxyacetone	6.90	15.20
Isobutane	0.41	0.55
Isobutylene	3.13	--
Isoprene	0.59	--
Isopropanol	0.91	1.39
Isopropyl acetate	0.71	1.31
Isopropyl chloride	0.68	0.98
Isovaleraldehyde	0.64	2.19
Mesityl oxide	1.09	3.14
Methacrolein	1.20	3.49
Methacrylic acid	0.82	1.06
Methanol	4.39	2.01
Methoxy-ethanol, 2-	2.25	3.13
Methyl acetate	1.74	1.85
Methyl acetylene	0.61	6.79
Methyl chloride	1.44	1.84
Methyl ethyl ketone	0.64	1.12
Methyl formate	3.11	1.94
Methyl methacrylate	0.99	2.42
Methyl-2-pentanol, 4-	1.66	2.00
Methyl-2-pentanone, 4-	0.56	1.63
Methyl-3-butyn-2-,2	0.59	--
Methyal	1.37	1.46
Methylaniline, N-	4.64	9.46
Methylcyclohexane	0.48	0.84
Methylcyclohexene, 1-	0.44	2.79
Methylpentynol	1.17	3.42
Methylstyrene, A-	13.90	--
Morpholine	0.92	2.59
Nitrobenzene	--	0.01
Nitroethane	1.40	3.45
Nitromethane	3.52	7.60
Nitropropane	1.05	2.02
Nonane-n	1.54	11.10
Octane	1.03	2.11
Pentane	0.52	0.63
Picoline,2-	0.43	1.18
Propane	0.55	0.60
Propionaldehyde	1.14	1.71
Propionic acid	1.30	5.08
Propyl alcohol	0.93	1.74
Propylbenzene, n-	0.51	--
Propylene	0.77	1.74
Propylene oxide	0.83	1.15
Pyridine	0.47	1.16

Compound Name	Response Factor[a]	
	FID	Catalytic Combustion
Styrene	4.22	--
Tetrachloroethane, 1,1,1,2	4.83	6.91
Tetrachloroethane, 1,1,2,2	7.89	25.40
Tetrachloroethylene	2.97	--
Toluene	0.39	--
Trichlorobenzene, 1,2,4-	0.80	2.40
Trichloroethane, 1,1,2-	1.25	3.69
Trichloroethylene	0.95	3.93
Trichloropropane, 1,2,3-	0.96	1.99
Triethylamine	0.51	1.48
Vinyl acetate	1.27	5.91
Vinyl chloride	0.84	1.06
Vinyl propionate	1.00	1.21
Vinylidene chloride	1.12	2.41
Xylene, p-	2.12	7.87
Xylene, m-	0.40	5.87
Xylene, o-	0.43	1.40

(a) Only a single analyzer of each type was evaluated (Foxboro/Century OV-108 FID and Bacharach TLV Sniffer - (Catalytic Combustion). Data from Reference 9 (revision of Reference 6) are used.

APPENDIX C

IONIZATION POTENTIALS (eV) FOR SOME COMMON INDUSTRIAL CHEMICALS[a]

Acetaldehyde	10.21
Acetamide	9.77
Acetic acid	10.37
Acetone	9.69
Acetonitrile	12.22
Acetophenone	9.27
Acetyl bromide	10.55
Acetyl chloride	11.02
Acetylene	11.41
Acrolein	10.10
Acrylonitrile	10.91
Allyl alcohol	9.67
Ammonia	10.15
Aniline	7.70
Anisole	8.22
Benzaldehyde	9.53
Benzene	9.25
Benzenethiol	8.33
Benzonitrile	9.71
Benzotrifluoride	9.68
Biphenyl	8.27
Bromine	10.55
Bromobenzene	8.98
1-bromobutane	10.13
2-bromobutane	9.98
1-bromopentane	10.10
1-bromopropane	10.18
2-bromopropane	10.08
1-bromopropene	9.30
3-bromopropene	9.70
2-bromothiophene	8.63
m-bromotoluene	8.81
o-bromotoluene	8.79
p-bromotoluene	8.67
Butane	10.63
1,3-butadiene	9.07
2,3-butadione	9.23
1-butanethiol	9.14
1-butene	9.58
cis-2-butene	9.13
trans-2-butene	9.13
3-butene nitrile	10.39
n-butyl acetate	10.01
sec-butyl acetate	9.91
n-butyl alcohol	10.04
n-butyl amine	8.71
s-butyl amine	8.70
t-butyl amine	8.64
n-butyl benzene	8.69
s-butyl benzene	8.68
1-bromo-2-chloroethane	10.63
Bromochloromethane	10.77
1-bromo-4-fluorobenzene	8.99
1-bromo-2-methylpropane	10.09
2-bromo-2-methylpropane	9.89
n-butyronitrile	11.67
t-butyl benzene	8.68
n-butyl formate	10.50
1-butyne	10.18
n-butyraldehyde	9.86
n-butyric acid	10.16
Carbon dioxide	13.79
Carbon monoxide	14.01
Chlorine	11.48
Chlorobenzene	9.07
1-chlorobutane	10.67
2-chlorobutane	10.65
1-chloro-2-fluorobenzene	9.16
1-chloro-3-fluorobenzene	9.21
1-chloro-2-methylpropane	10.66
2-chloro-2-methylpropane	10.61
1-chloropropane	10.82
2-chloropropane	10.78
3-chloropropene	10.04
2-chlorothiophene	8.68
m-chlorotoluene	8.83
o-chlorotoluene	8.83
p-chlorotoluene	8.70
Crontonaldehyde	9.73
Cyanogen	13.80

Cyclohexane	9.98
Cyclohexanone	9.14
Cyclohexene	8.95
Cyclo-octatetraene	7.99
Cyclopentane	10.53
Cyclopentanone	9.26
Cyclopentene	9.01
m-dichlorobenzene	9.12
o-dichlorobenzene	9.07
p-dichlorobenzene	8.94
1,2-dichloroethane	11.12
cis-dichloroethene	9.65
trans-dichloroethene	9.66
Diborane	12.10
Dichloromethane	11.35
1,2-dichloropropane	10.87
1,3-dichloropropane	10.85
2,3-dichloropropene	9.87
Dibutyl amine	7.69
Diethoxymethane	9.70
N,N-diethyl acetamide	8.60
Diethyl amine	8.01
Diethyl ether	9.53
N,N-diethyl formamide	8.89
Diethyl ketone	9.32
Diethyl sulfide	8.43
Diethyl sulfite	9.68
Dihydropyran	8.34
1,1-dimethoxyethane	9.65
Dimethoxymethane	10.00
Diiodomethane	9.34
Diisopropylamine	7.73
N,N-dimethyl acetamide	8.81
Dimethyl amine	8.24
Cyclopropane	10.06
Dedaborane	11.00
Dibromochloromethane	10.59
Dibromodifluoromethane	11.07
1,1-dibromoethane	10.19
1,2-dibromoethane	9.45
Dibromomethane	10.49
1,3-dibromopropane	10.07
2,2-dimethyl butane	10.06
2,3-dimethyl butane	10.02
3,3-dimethyl butanone	9.17
Dimethyl ether	10.00
N,N-dimethyl formamide	9.12
2,2-dimethyl propane	10.35
Dimethyl sulfide	8.69
p-dioxane	9.13
Dipropyl amine	7.84
Dipropylsulfide	8.30
Durene	8.03
Ethane	11.65
Ethanethiol	9.29
Ethene	10.52
Ethyl acetate	10.11
Ethyl alcohol	10.48
Ethyl amine	8.86
Ethyl benzene	8.76
Ethyl bromide	10.29
Ethyl chloride	10.98
Ethyl disulfide	8.27
Ethylene oxide	10.57
Ethyl formate	10.61
Ethyl iodide	9.33
Ethyl isothiocyanate	9.14
Ethyl methyl sulfide	8.55
Ethyl nitrate	11.12
Ethyl propionate	10.00
Ethyl thiocyanate	9.89
Ethynylbenzene	8.82
Fluorine	15.70
Fluorobenzene	9.20
o-fluorophenol	8.66
m-fluorotoluene	8.92
o-fluorotoluene	8.92
p-fluorotoluene	8.79
Formaldehyde	10.87
Formamide	10.25
Formic acid	11.05
Freon 11 ($CFCl_3$)	11.77
Freon 12 (CF_2Cl_2)	12.91
Freon 13 (CF_3Cl)	12.91
Freon 22 ($CHClF_2$)	12.45
Freon 113 (CH_3CCl_3)	11.78
2-furaldehyde	9.21
Furan	8.89
Hexane	10.18
Heptane	10.08
2-heptanone	9.33
1-hexene	9.46
Hydrogen	15.43
Hydrogen bromide	11.62
Hydrogen chloride	12.74
Hydrogen cyanide	13.91
Hydrogen fluoride	15.77
Hydrogen iodide	10.38
Hydrogen selenide	9.88
Hydrogen sulfide	10.46
Hydrogen telluride	9.14
Iodine	9.28

Iodobenzene	8.73
1-iodobutane	9.21
2-iodobutane	9.09
1-iodo-2-methylpropane	9.18
2-iodo-2-methylpropane	9.02
1-iodopentane	9.19
1-iodopropane	9.26
2-iodopropane	9.17
o-iodotoluene	8.62
m-iodotoluene	8.61
p-iodotoluene	8.50
Isobutane	10.57
Isobutyl amine	8.70
Isobutyl acetate	9.97
Isobutyl formate	10.46
Isobutyraldehyde	9.74
Isobutyric acid	10.02
Isopentane	10.32
Isoprene	8.85
Isopropyl acetate	9.99
Isopropyl alcohol	10.16
Isopropyl amine	8.72
Isopropyl benzene	8.69
Isopropyl ether	9.20
Isovaleraldehyde	9.71
2,3-lutidine	8.85
2,4-lutidine	8.85
2,6-lutidine	8.85
Mesitylene	8.40
Mesityl oxide	9.08
Methane	12.98
Methanethiol	9.44
N-methyl acetamide	8.90
Methyl acetate	10.27
Methyl alcohol	10.85
Methyl amine	8.97
Methyl bromide	10.53
2-methyl-1-butene	9.12
3-methyl-1-butene	9.51
3-methyl-2-butene	8.67
Methyl butyl ketone	9.34
Methyl butyrate	10.07
Methyl chloride	11.28
Methylcyclohexane	9.85
4-methylcyclohexene	8.91
Methyl disulfide	8.46
Methyl ethyl ketone	9.53
Methyl formate	10.815
2-methyl furan	8.39
Methyl iodide	9.54
Methyl isobutyl ketone	9.30
Methyl isobutyrate	9.98
Methyl isopropyl ketone	9.32
Methyl isothiocyanate	9.25
1-methyl naphthalene	7.96
2-methyl naphthalene	7.96
2-methylpentane	10.12
3-methylpentane	10.08
2-methyl propene	9.23
Methyl propionate	10.15
Methyl propyl ketone	9.39
Methyl thiocyanate	10.07
a-methyl styrene	8.35
Naphthalene	8.12
Nitric oxide	9.25
Nitrobenzene	9.92
Nitrogen	15.58
Nitrogen dioxide	9.78
Nitroethane	10.81
Nitromethane	11.08
1-nitropropane	10.88
2-nitropropane	10.71
Oxygen	12.08
Ozone	12.08
Pentaborane	10.40
Pentane	10.35
2,4-pentanedione	8.87
1-pentene	9.50
Phenetole	8.13
Phenol	8.50
Phenyl isocyanate	8.77
Phenyl isothiocyanate	8.52
Phosgene	11.77
2-picoline	9.02
3-picoline	9.02
4-picoline	9.04
Propane	11.07
1-propanethiol	9.20
Propiolactone	9.70
Propionic acid	10.24
Propionitrile	11.84
Propionaldehyde	9.98
Propyl acetate	10.04
Propyl alcohol	10.20
Propyl amine	8.78
Propyl benzene	8.72
Propylene	9.73
Propylene oxide	10.22
Propyl ether	9.27
Propyl formate	10.54
Propyne	10.36
Pyridine	9.32

Pyrrole	8.20	Triethylamine	7.50
Styrene	8.47	Trimethyl amine	7.82
Thiolacetic acid	10.00	2,2,4-trimethyl pentane	9.86
Thiophene	8.86	Tripropyl amine	7.23
Tetrachloroethene	9.32	Valeraldehyde	9.82
Tetrachloromethane	11.47	Valeric acid	10.12
Tetrahydrofuran	9.54	Vinyl acetate	9.19
Tetrahydropyran	9.26	Vinyl bromide	9.80
Toluene	8.82	Vinyl chloride	10.00
Tribromoethene	9.27	Vinyl methyl ether	8.93
Tribromofluoromethane	10.67	Water	12.59
Tribromomethane	10.51	m-xylene	8.56
Trichloroethene	9.45	o-xylene	8.56
Trichloromethane	11.42	p-xylene	8.45

(a) From AID Model 580 product manual.